Comparison Between the Activities of CoMo and CoW Catalyst for SWNT Poduction by CO Disproportionation
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Beamline(s): X18B

Introduction: Single-wall carbon nanotubes (SWNT) can be considered as one of the building blocks for nanoscale science and nanotechonology. The procedures used thus far for SWNT production include arc discharge, laser ablation and catalytic decomposition of a carbon-containing molecule (sometimes referred to as chemical vapor deposition) over a metal catalyst. Our group has focused on the disproportionation of CO on several bimetallic catalysts, which exhibited a high selectivity towards the production of SWNT at relatively low temperatures. Among the various formulations investigated we previously reported that a Co-Mo catalysts supported on silica gel and having low Co:Mo ratios exhibited the best performance The Co-Mo system is a commonly applied catalyst for hydrotreating process, addition of W to this bimetallic catalyst increases the hydrotreating activity significantly and active phases similar to the so-called CoMoS have been reported. However, a Co promoted W catalyst is generally regarded as an unsuccessful combination for hydrotreating. Reports of supported pure CoW catalyst are scarce and the reason for the lack of synergy between Co and W in the sulfide state is still unclear. In the present contribution we have turn our attention to the CoW catalytic system for SWNT production and have designed a characterization strategy on the basis of the abundant precedent literature and our own work on the application of these techniques to investigate this bimetallic system. We have been able to put together a detailed picture of the structure of this catalyst, and built up analogy with the Co Mo catalytic system, which can be used to explain the variations in selectivity towards SWNT observed when the catalyst formulations, pretreatment and (or) reaction conditions are changed.

Methods and Materials The ability different catalysts to produce SWNT by CO disproportionation were tested by passing pure CO over the catalyst at 850ºC. The characterization of the carbon deposits was done by Raman spectroscopy, TEM and TPO. The X-ray absorption data were obtained at the National Synchrotron Light Source at Brookhaven National Laboratory, using beam line X-18B. The EXAFS experiments were conducted in a stainless steel sample cell at liquid nitrogen temperature. Six scans were recorded for each sample. The spectra of Co_3O_4, CoO, and $CoWO_4$ as well as Co foil were obtained at liquid nitrogen temperature and used as references.

Results: Figure 1 compares the XANES spectra for the K-edge of Co (E_o = 7709eV) in two calcined Co:W(1:3)/SiO_2 and Co:Mo(1:3)/SiO_2 catalysts and those in the $CoWO_4$ and $CoMoO_4$ references. Except for some difference in the intensity of the first peak in the edge, the spectra look remarkably similar. In agreement with results obtained by UV/VIS DR and Raman spectroscopy it is clear that in a catalyst with low Co:W (Mo) molar ratio cobalt is interacting strongly with either W or Mo in a local environment similar to $CoWO_4$ or $CoMoO_4$. By contrast, the Co edge for the Co:W (2:1) and CoMo(2:1) catalysts that contain excess Co are very different from that of the cobalt tungstate (molybdate) reference. As shown in Fig. 2, the XANES of these catalysts are in fact very similar to that of Co_3O_4. The EXAFS data was in good agreement with the conclusions reached from XANES analysis. As shown, in Fig. 3, the Fourier Transform for the calcined catalyst becomes very similar to that of Co_3O_4 as the loading of W decreases, indicating that this oxide is the predominant form present when the loading of W is scarce. In previous works, we proposed that for the CoMo system the role of Co is the activation of CO. However, when it is in the form of large metal aggregates, it has the tendency to generate mostly MWNT, carbon filaments and graphite. We reported that when Mo is present in the catalyst and there is no Co in excess, a well-dispersed Co+2 species in the form of a Co molybdate-like phase is stabilized. From the detailed studies conducted over the CoW system reported in this contribution, we can propose that the formation of a similar interacting Co tungstate-like species plays a determinant role in the catalytic activity towards the formation of SWNT.

Conclusions As previously shown for the case of the Co-Mo system, the selectivity of the Co-W catalysts towards SWNT production by CO disproportionation strongly depends on the stabilization of Co2+ species, which results from an interaction with W. The extent of this interaction is inversely proportional to the Co:W molar ratio. It was also found that the selective catalyst in the oxidic state is composed by W forming small clusters in the form of well dispersed W (6+) species and Co is interacting with Mo in a superficial Co tungstate-like structure

References: J. E. Herrera, L. Balzano, A. Borgna, W. E. Alvarez, D. E. Resasco "Relationship Between the Structure/Composition of Co-Mo Catalysts and their Ability to Produce Single-Walled Carbon Nanotubes by CO Disproportionation" Journal of Catalysis 204 (2001) 129-145

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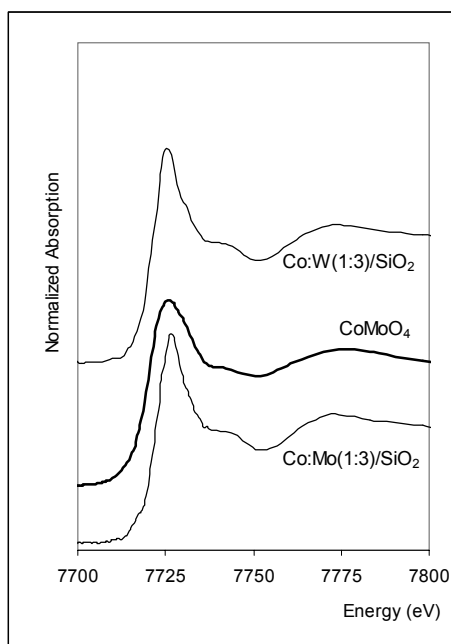
Figure 1. Co K edge (7,709 eV) XANES of calcined CoW(1:3)/SiO2 and Co:Mo(1:3)/SiO2 catalysts compared to CoWO4 and CoMoO4 used as a references.
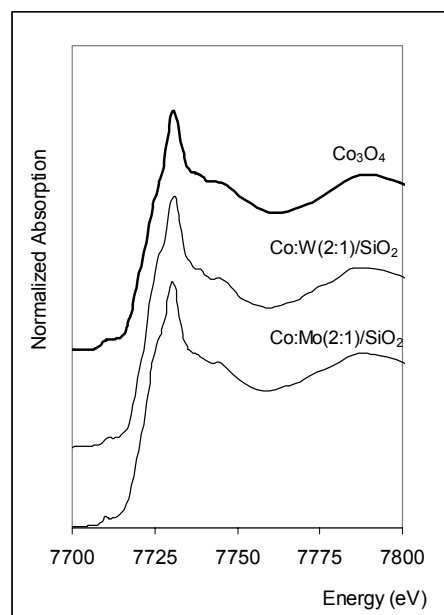

Figure 2 Co K edge XANES of a calcined CoW(2:1)/SiO2 and Co:Mo(2:1)/SiO2 catalysts compared to Co3O4 reference.
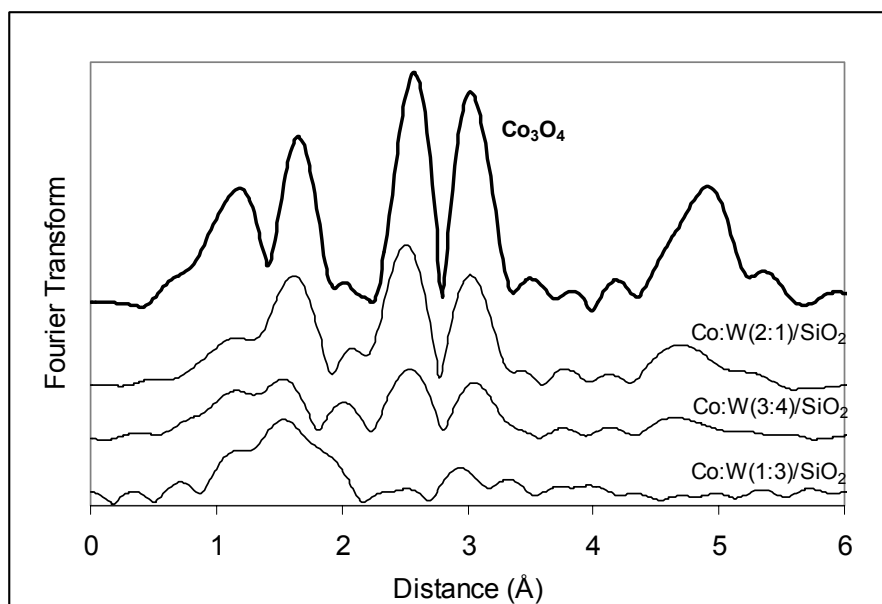

Figure 3. Fourier transforms of the k3 EXAFS data of the Co K edge obtained on the calcined CoW(1:3)/SiO2 , CoW(3:4)/SiO2 and CoW(2:1)/SiO2 catalysts and for Co3O4 reference.